

N 9 2 - 2 1 6 2 2

PROCESSING Bi-Pb-Sr-Ca-Cu-O SUPERCONDUCTORS FROM AMORPHOUS STATE

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ABSTRACT

The bismuth-based high- $T_C$  superconductors can be processed via an amorphous Bi-Pb-Sr-Ca-Cu oxide. The amorphous oxides were prepared by melting the constituent powders in an alumina crucible at 1200°C in air followed by pouring the liquid onto an aluminum plate, and rapidly pressing with a second plate. In the amorphous state, no crystalline phase was identified in the powder X-ray diffraction pattern of the quenched materials. After heat treatment at high temperature the amorphous materials crystallized into a glass-ceramic containing a large fraction of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase ( $T_C=110\text{K}$ ). The processing method, crystallization, and results of dc electrical resistivity and ac magnetic susceptibility measurements are discussed.

1. INTRODUCTION

The Bi-based system of high  $T_C$  superconductors can be prepared by forming an amorphous oxide followed by heat treatment [1-7]. The amorphous state of the oxides, also known as glasses, are defined by an amorphous x-ray diffraction pattern (Figure 1). Preparation of high  $T_C$  superconductors using the glass technology has many technological advantages such as homogeneity, fine-grained microstructure, reduced segregation, and extended solid solubility. The glass can be molded into various shapes, or used as a thick film coating. To exploit these

advantages, it is important to provide an understanding of the microstructure and phase formation in the complicated processing of these superconductors. A particular goal is to maximize the formation of the high-temperature ( $T_C > 100\text{K}$ ) phase.

Three starting compositions: 1)  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{1.25}\text{Ca}_{1.75}\text{Cu}_2\text{O}_x$  (G1), 2)  $\text{Bi}_2\text{PbSr}_2\text{Ca}_2\text{Cu}_4\text{O}_x$  (G2), 3)  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$  (G3) were studied. The compositions with addition of Pb were selected to promote the formation of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase [7-9]. The formation of the crystalline phases depends on the temperature, atmosphere and length of the heat treatment time. We have performed an extensive heat treatment study to identify those crystalline phases [8,9]. It is found that the phase formation is very complicated and very sensitive to the starting composition.

In this paper, we show that a Bi-based high  $T_C$  superconductor can be processed from an amorphous state. Both superconducting and non-superconducting oxide phases are crystallized through subsequent heat treatments. After heat-treatment, the superconductor contains a large fraction of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase.

## 2. EXPERIMENTAL

Amorphous oxides were prepared from as-received analytical grade powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$ . The stoichiometric oxide powders were well mixed with mortar and pestle. The powder was first calcined at  $800^\circ\text{C}$  for 20 hours. The calcined powder was heated to  $1200^\circ\text{C}$  in alumina crucibles to form a liquid. The viscous liquid was held at  $1200^\circ\text{C}$  for about 10 minutes and stirred occasionally. The liquid was quenched to room temperature onto one aluminum plate and rapidly pressed with another plate to in order to preserve the amorphous state.

Differential thermal analysis (DTA) was carried out on the amorphous oxides in order to determine the temperatures at which crystallization would occur. The DTA traces were obtained using a commercial system equipped with a computer [9]. Powdered samples were placed in an alumina sample holder and measured in air.

The heat treatment of the samples was guided by DTA, DSC, and on-line resistivity measurements. The heat-treatment temperature varied from  $400^\circ\text{C}$  to  $900^\circ\text{C}$ . The length of heat treatment ranged from 30 minutes to 15 days. The heat treatments were carried out in air, as well as in controlled atmospheres of nitrogen, an oxygen-nitrogen mixture, and oxygen [8,9]. The electrical resistivity of the oxide was used to monitor the change of the electrical properties of the oxide (Figure 2). In this experiment, the resistivity of a sample with four-leads attached was measured at room temperature after annealing at fixed temperature for one hour. The measurement was repeated from room temperature to  $850^\circ\text{C}$  using the same sample.

X-ray powder diffraction patterns were used to identify the crystalline oxide phases formed after a heat treatment. The pattern was measured on powdered samples at room temperature with  $\text{CuK}\alpha_1$  radiation. Sample preparation followed the methods described by McMurdie [10].

Electrical resistivity and ac magnetic susceptibility were measured as a function of temperature from 295K to 20K. Alternating-current magnetic susceptibility was measured using a computerized ac magnetometer with applied ac voltage at 1.68 kHz and ac field at 0.5 gauss. The electrical resistivity was measured using a standard four-probe dc technique. Bar-like samples of 1.5mm x 1.5mm x 8mm were used. Currents from 0.01 $\mu$ A to 10 mA were used for the resistivity measurements.

### 3. RESULTS AND DISCUSSION

#### a. Amorphous State of Bi-Pb-Sr-Ca-Cu Oxide:

The amorphous state is characterized by an amorphous x-ray diffraction pattern as shown in Figure 1. The pattern has two broad scattering bands ( $2\theta = 29^\circ$ ) and no sharp crystalline peaks above the amorphous curve. In Figure 1, the small peak at  $2\theta \approx 44^\circ$  is a residual crystalline oxide. The material remained amorphous as long as the temperature never rose above the glass transition temperature,  $T_g$ , where the material changes from an amorphous to a crystalline state (Figure 2). The  $T_g$  of the glasses determined from the data of DTA and DSC data is in the range from 400°C to 450°C.

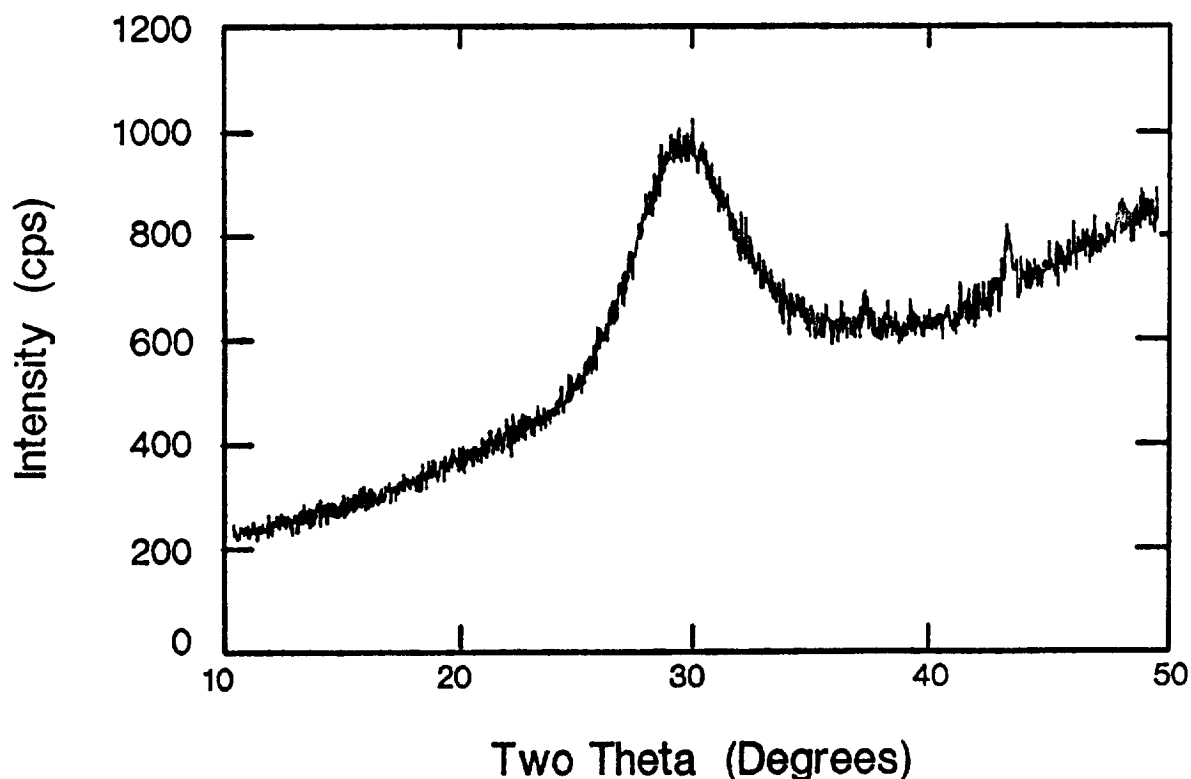


Figure 1. The x-ray powder patterns of the as-quenched Bi-Pb-Sr-Ca-Cu-O oxide (G3).

The microanalysis of the amorphous oxide with a scanning electron microscopy showed that the composition of the sample was uniform. The compositional analysis was done across the thickness, approximately 400  $\mu\text{m}$ , of an as-quenched amorphous oxide, using a 6  $\mu\text{m}$  diameter beam. Further analysis of the SEM data with a crushed sample having particles less than  $\approx 0.1\mu\text{m}$  indicated that the amorphous sample is locally heterogeneous.

The amorphous oxide showed no evidence of superconductivity based on electrical resistivity and ac susceptibility measurements from room temperature to 20K.

#### b. Crystallization Processes:

Crystallization occurs when the amorphous Bi-Pb-Sr-Ca-Cu oxides are heated above the glass transition temperature. Details of the x-ray characterization of the crystallization process are reported elsewhere.[8,9]

The crystallization process for the three compositions can be divided into two temperature ranges based on the thermal analysis data. The DTA curve for the glass G2 is illustrated in Figure 2. In the temperature range from 400°C to 700°C, DTA traces of the glasses reveal many exothermal peaks. These peaks are associated with the thermal energy released while forming crystalline phases of CaO, Cu<sub>2</sub>O, CaPbO<sub>3-x</sub>, Ca<sub>2</sub>CuO<sub>3</sub>, SrCO<sub>3</sub>, Ca<sub>2</sub>PbO<sub>4</sub>, and (Bi,Pb)<sub>2.2+y</sub>Sr<sub>1.8-y</sub>Cu<sub>1+y</sub>O<sub>x</sub>. These oxides are not desirable high T<sub>C</sub> superconducting phases.

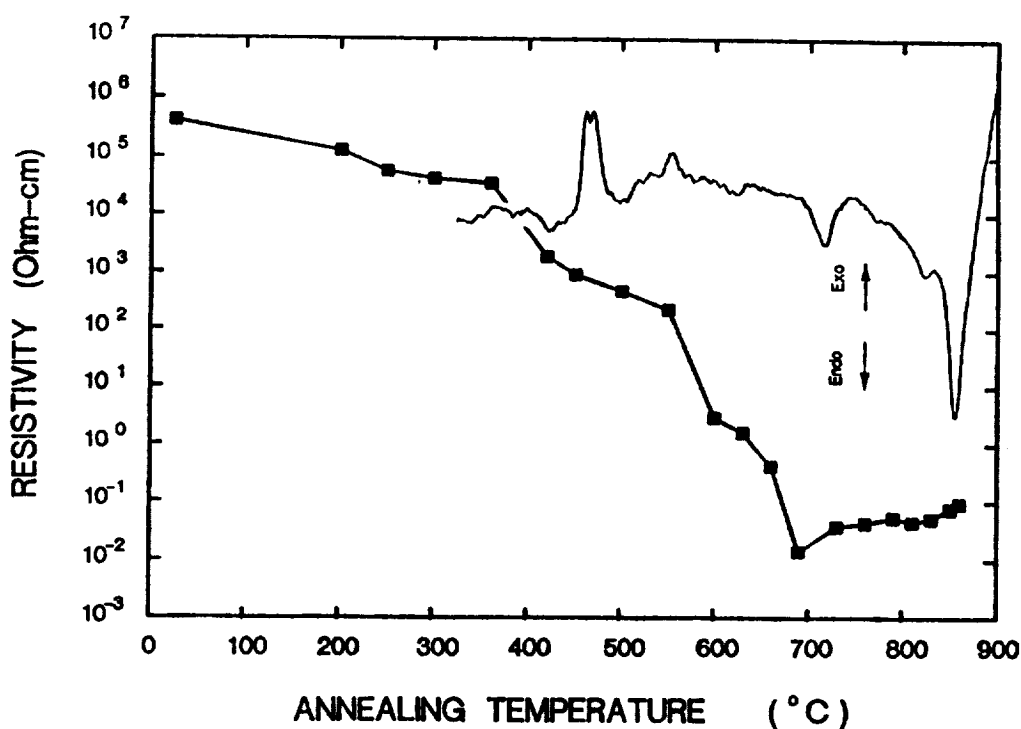


Figure 2. The room temperature resistivity as a function of annealing temperature, and DSC trace of as the Bi-Pb-Sr-Ca-Cu oxide, G2.

In the temperature range from 700°C to 900°C, several melting peaks (endothermic peaks) were observed in DTA traces. The crystalline phases found in this temperature range are  $(\text{Bi,Pb})_{2.2+y}\text{Sr}_{1.8-y}\text{Cu}_{1+y}\text{O}_x$ ,  $\text{Ca}_2\text{PbO}_4$ , and  $\text{CuO}$ ,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . The last two oxides are the superconducting phases whose critical temperatures are 80K and 110K, respectively. The endothermic peaks associated with forming these phases suggest that the formation of the superconducting phases is probably a product of a chemical reaction.

To obtain a superconducting phase, the heat treatment temperature for the amorphous Bi-Pb-Sr-Ca-Cu oxide are listed in Table 1. Note that starting with compositions G1 and G2, the major phase is  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ . After prolonged annealing at 850°C, the composition develops a nominal amount (less than 10%) of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase. However, starting from the composition G3, both  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  can be obtained. The fraction of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase increased with annealing time.

#### c. Electrical and Magnetic Properties:

The room temperature electrical resistivities of the amorphous oxides are very high, and vary according to the quench conditions.

TABLE I  
Temperature Range for Forming Superconducting Phases

Material	<u>Resulting Phases</u>	
	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ( $T_c = 80\text{K}$ )	$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ( $T_c = 110\text{K}$ )
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{1.25}\text{Ca}_{1.75}\text{Cu}_2\text{O}_x$	750°C-850°C	-----
$\text{Bi}_2\text{PbSr}_2\text{Ca}_2\text{Cu}_4\text{O}_x$	750°C-850°C	-----
$\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$	500°C-860°C	840°C-850°C

Figure 2 shows the decrease of the room temperature resistivity as a function of the heat treating temperature. A DTA curve was superimposed on the figure for comparison. In the vicinity of 410°C, a glass transition was observed electrically. Two step-like decreases of the electrical resistivity were observed at 550°C and 700°C which can be correlated to the DTA peaks and phase formation at same temperature range. Each phase formation or transition appears to result in the decrease of resistivity over one order in magnitude. After heat treatment at 850°C, the total decrease of the room temperature resistivity is nearly 8 orders of magnitude. The resistivity of the sample is at minimum at 750°C-780°C. But neither the sample with the minimum resistivity nor the sample after a on-line heating run show any superconductivity when measured down to 40K electrically.

Both DTA and the electrical monitoring studies reveal that the crystallization of the high  $T_C$  superconducting phases from the amorphous phase require proper temperature control and long annealing time. For single step processing in air, the most suitable conditions to form the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase is 72 hours at 850°C.

The x-ray diffraction patterns of the samples annealed for 72 hours at 850°C are shown in Figure 3 and 4. The detailed identification of these patterns were reported previously [8,9]. As far as high  $T_C$  superconducting phase is concern, the sample G1 and G2 are very similar. However, the peaks associated with the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase ( $2\theta=4.8^\circ$  and  $2\theta=24^\circ$ ) are significantly larger for the sample G3.

Figure 5 shows the electrical resistivity as function of temperature for the sample G1 after annealing at 850°C for 120 hour in air. The solid line in Figure 5 is the first derivative of the resistivity against temperature ( $dR/dT$ ). A peak in the  $dR/dT$  reflects the sharp decrease of resistivity which can be interpreted as a phase transition if part of the sample is superconducting. A large peak at 80K agrees with the large superconducting phase and a small peak at 110K is consistent with the small amount (less the 5%) of non-continuous  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase.

Figure 6 shows the electrical resistivity as function of temperature for the annealed sample G3 whose x-ray pattern is shown in Figure 4. The zero resistivity near 100K indicates that  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  is continuous throughout the sample. The ac susceptibility of the annealed G3, shown in Figure 7, indicates that the fraction of the sample that is superconducting at 110K is about 50%, i.e. 50% of the annealed material is the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phase.

In conclusion, we processed the Bi-based high  $T_C$  superconductors from the amorphous state. The glasses transform into polycrystalline ceramics upon heat treatment at high temperatures. Heat treatments below 700°C produces various non-superconducting oxides. Heat treatments between 750°C and 850°C produce the superconducting  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  phases. The former phase formed easily from all three composition with short heat treatment times. The latter phase can be formed only in the composition G3 and after prolonged heat treatment.

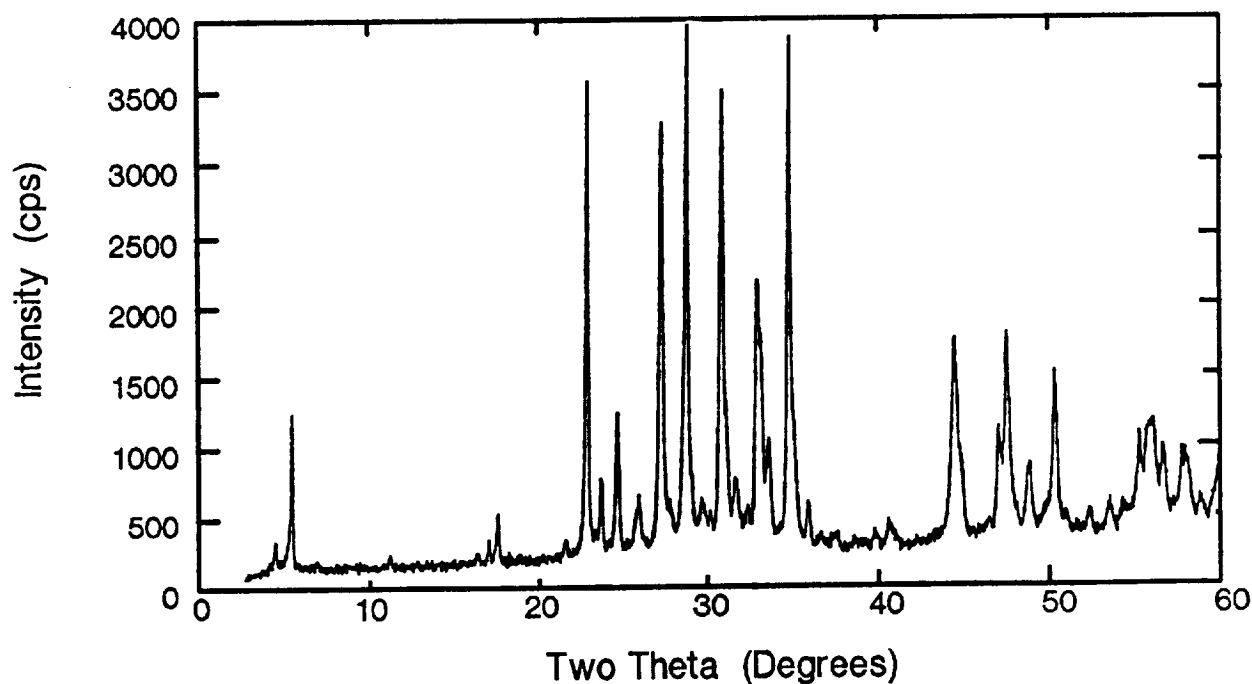


Figure 3. X-ray powder diffraction pattern of the Bi-Pb-Sr-Ca-Cu oxide, G2, after annealing at 850°C for 71 hours in air.

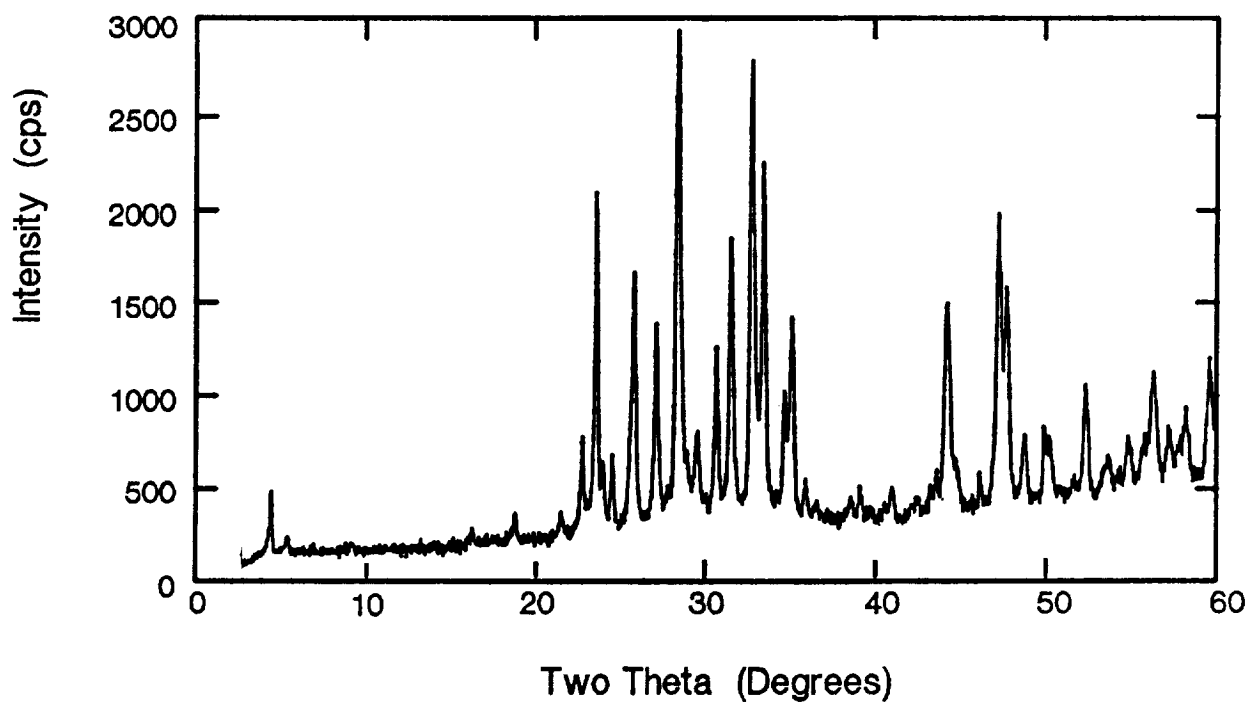


Figure 4. X-ray powder diffraction pattern of the Bi-Pb-Sr-Ca-Cu oxide, G3, after annealing at 850°C for 76 hours in air.

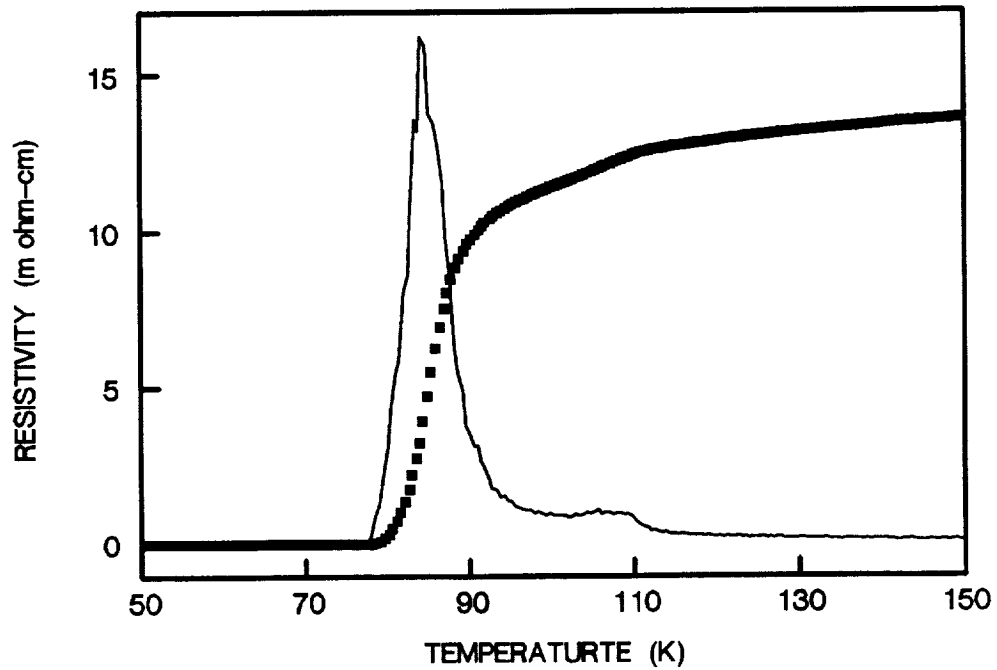


Figure 5. The resistivity of the Bi-Pb-Sr-Ca-Cu oxide, G1, as a function of temperature (heat treated at 850°C for 120 hours in air). The solid curve is the  $dR/dT$  to show the transition temperature.

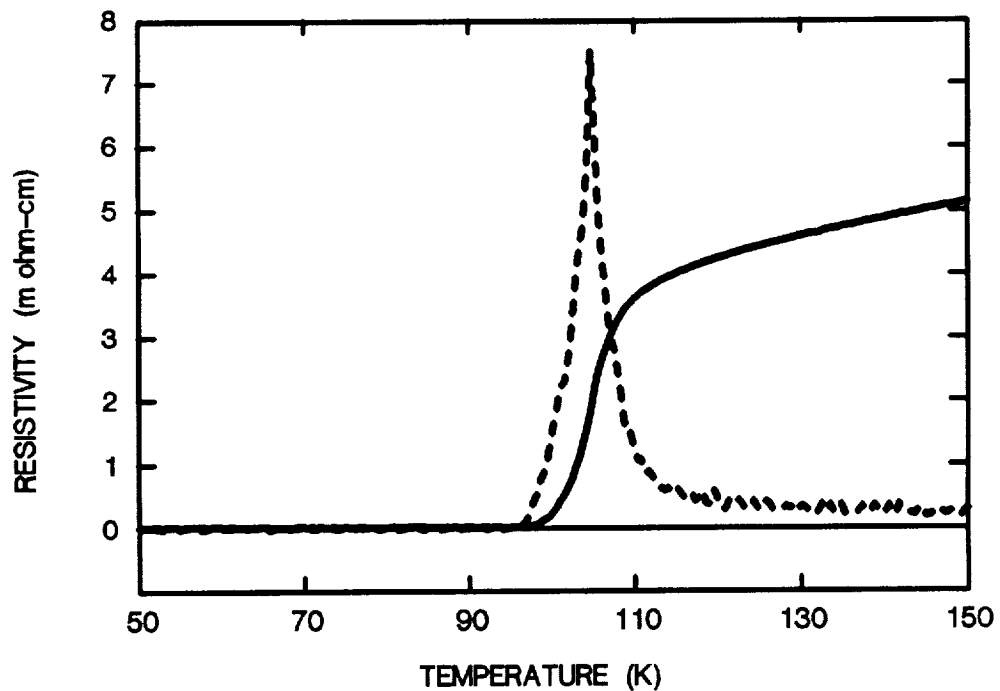


Figure 6. The resistivity of the Bi-Pb-Sr-Ca-Cu oxide, G3, as a function of temperature (heat treated at 850°C for 76 hours in air). The dashed curve is the  $dR/dT$  to show the transition temperature.

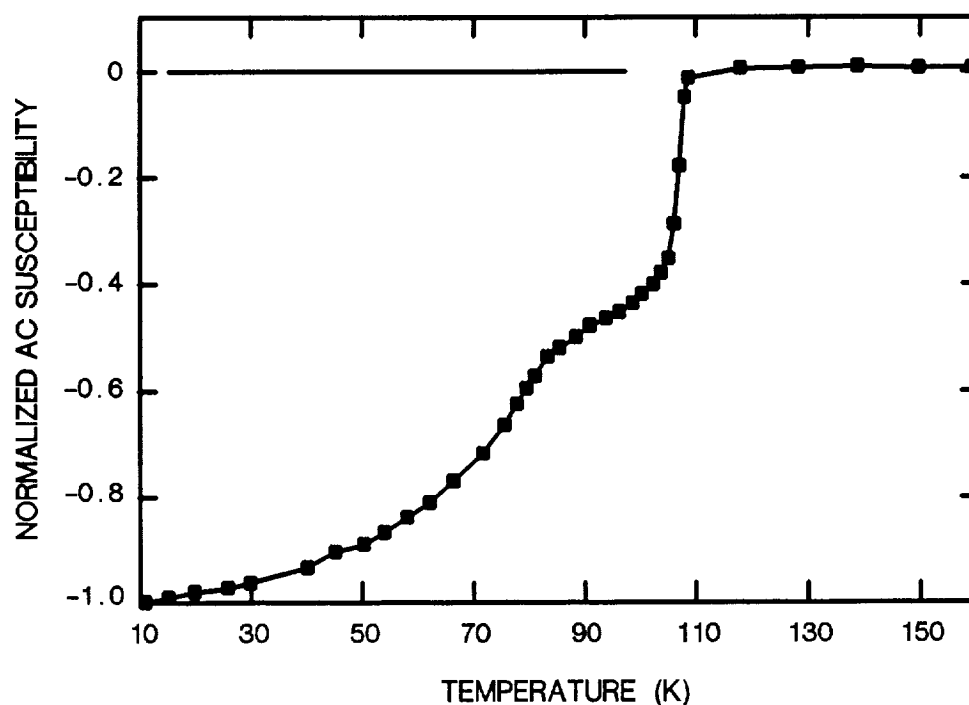


Figure 7. The ac susceptibility of the Bi-Pb-Sr-Ca-Cu oxide, G3, as a function of temperature (heat treated at 850°C for 76 hours in air).

#### ACKNOWLEDGEMENT

We like to acknowledge D. Kauffman for assistance in melting the glasses and R. Drew and D. Mathews for measuring the ac susceptibility.

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